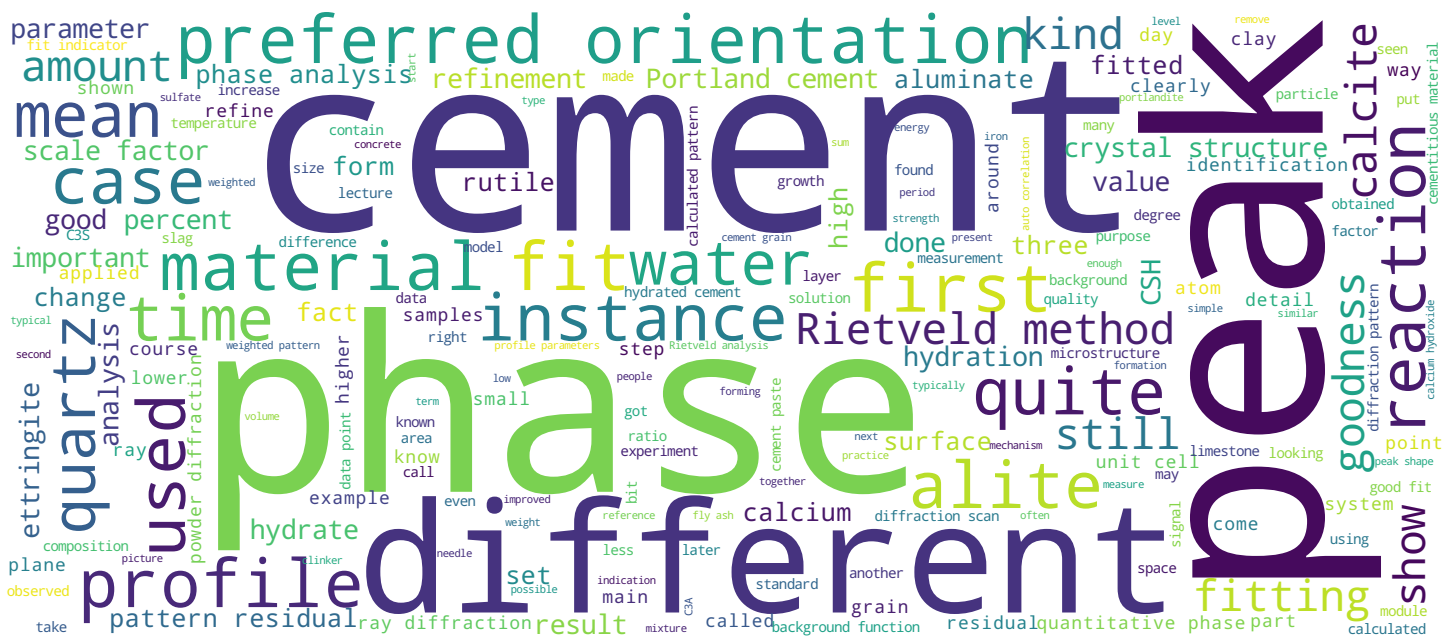


The Rietveld method

Cement Chemistry and Sustainable Cementitious Materials

Dr. Ruben Snellings



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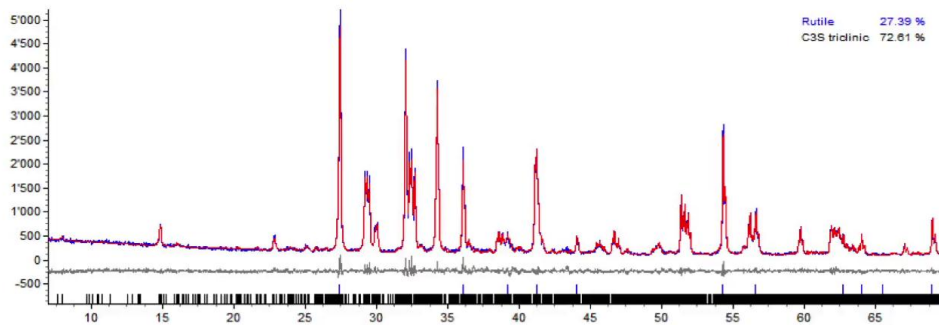
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The Rietveld method

- Rietveld (1969): diffraction pattern analysis by a curve fitting procedure
- First proposed for neutron diffraction
- Least-squares minimization between observed and calculated profiles
- Extended to XRD profiles in the 1970's



Hugo Rietveld (1932-2016)



Before we dive into quantitative phase analysis, we should first introduce the main method used for this purpose, "The Rietveld Method". This lecture describes the basic principles of the method, and builds further on the insights into x-ray powder diffraction that have been treated in lecture two. The Rietveld method was originally developed by Hugo Rietveld in the late 60s. This was done for the refinement of crystal structures using neutron powder diffraction. Only later in the 70s, it was extended to X-rays and even later, like in the 80s, it was eventually extended to quantitative phase analysis. For cement analysis, the first application of the Rietveld method date back to the early 90s.

Notes

Summary



0m 04s

- **Phase identification** (crystalline and amorphous)
- Crystal structure refinement
- Crystal structure determination (not trivial)
- **Quantitative phase analysis**
- Microstructural analyses (crystallite size – microstrain)

Kinetic studies

Thermal expansion

Polymorphism

In-situ chemistry

Phase transitions

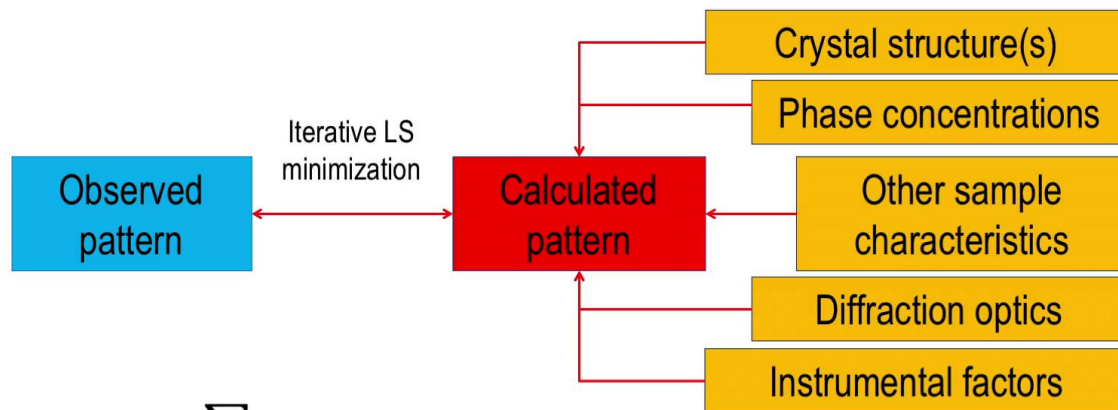
The Rietveld method now finds its use in a wide variety of areas as a characterization technique for crystalline solids. Next to its use in quantitative phase analysis, the method can be used to derive or refine crystal structures for pure powder samples. Also, crystallite size and strain can be determined through peak shape analysis. In fact, many key properties of solid systems can be studied by Rietveld analysis. Kinetic studies for instance of reactions occurring during cement hydration or polymorph transitions, thermal expansion, behaviour of ceramics, in-situ chemistry, and phase transitions can be analyzed easily using the Rietveld method.

Notes

Summary



The Rietveld method



$$S_y = \sum_i w_i (y_i(obs) - y_i(calc))^2$$

$$y_i(calc) = \sum_{j=1}^{Nphases} S_j \sum_{k=1}^{Npeaks} Lp_k |F_{k,j}|^2 G_j(2\theta_i - 2\theta_{k,j}) A_j P_{k,j} + bkg_i$$

To do this, the Rietveld method minimizes the difference between observed and calculated patterns at each data point i , in the diffraction pattern using the least squares approach. Here the sum of the statistically weighted squared differences between the observed and calculated intensities is minimized over the whole pattern. The calculated pattern takes into account crystal structure information, phase concentrations, and other sample characteristics such as micro texture but also diffraction optics and instrument dependent parameters such as X-ray source etc. are being taken into account when calculating the X-ray powder diffraction pattern.

Notes

Summary



1m 34s

The Rietveld method

$$y_i(\text{calc}) = \sum_{j=1}^{N_{\text{phases}}} S_j \sum_{k=1}^{N_{\text{peaks}}} Lp_k |F_{k,j}|^2 G_j(2\theta_i - 2\theta_{k,j}) A_j P_{k,j} + bkg_i$$

- The intensity $y_i(\text{calc})$ at 2θ angle i is determined by:
 - **background** contribution
 - **overlapping diffraction peaks** depending on:
 - diffraction **intensities** of the individual peaks
 - peak **shape** and peak **position** with respect to i

The calculated intensity at a given data point in the diffraction scan is obtained as the sum of the contribution of the background and all neighbouring reflections B of phases J in your sample. This is also expressed in the mother equation of the Rietveld method shown here. Here, one can see that S of j is the scale factor, Lp , is a Lorentz polarization factor, F is a structure factor, G is the peak shape function, A the x-ray absorption coefficient, and P the preferred orientation correction. In lecture two, we have treated each of these factors in more detail, and we have explained what is the physical basis of these factors.

Notes

Summary



What is a good fit?

- Need to monitor progress of fit
- Need to compare different model fits
- Need to measure data quality

Agreement tests

- **Visual inspection of fit**
- **Numerical factors**
 - R-factors
 - 'Goodness of fit'
 - Durbin-Watson statistic
- **Monitoring of chemical parameters**
 - Bond lengths and angles for structure refinements



Now before we go into a demonstration and practice, it is worthwhile to reflect on what we really can call a good fit and how we can actually evaluate this. This is needed because we want to check that we are going in the right way when doing the fitting. And there is also a need to be able to compare between different measures of goodness of fit and maybe we also want to be able to do this independent of the quality of the data. To this purpose, the most direct way of checking if a fit is good or going the right way is by actual visual inspecting. All this is by any means the most powerful and direct way of evaluation, it is also the most subjective way. What is for instance good in one student's eyes, may not be so good for his supervisor. Numerically assessed fitting, several numerical parameters, or factor, or initials are available. Depending on the material itself, the data quality, and the purpose of the analysis, one may prefer to use residual, or R-factors, or the chi or goodness of fit indicator, or for instance the Durbin-Watson statistic. Sometimes, a very good fit is obtained by allowing very large shifts in crystallographic parameters such as unit cell parameters, or increase of structure refinements atomic positions.

Notes

Summary



3m 12s

What is a good fit?

- Need to monitor progress of fit
- Need to compare different model fits
- Need to measure data quality

Agreement tests

- **Visual inspection of fit**
- **Numerical factors**
 - R-factors
 - 'Goodness of fit'
 - Durbin-Watson statistic
- **Monitoring of chemical parameters**
 - Bond lengths and angles for structure refinements



In these cases, it is good practice to always check whether the obtained crystal structure is chemically reasonable. For instance, it is known from a great many of experimental data and from chemical bond theory, that a tetrahedral silicon oxygen bond should have a length of about 1.6 angstroms. Very large deviations, for instance 1.8 angstroms, are therefore quite suspicious and would require further analysis and verification.

Notes

Summary



4m 37s

The Rietveld method

$$R_p = \frac{\sum |y_i(obs) - y_i(calc)|}{\sum y_i(calc)} \quad (\text{'R-pattern'})$$

$$R_{wp} = \left\{ \frac{\sum w_i (y_i(obs) - y_i(calc))^2}{\sum w_i (y_i(obs))^2} \right\}^{1/2} \quad (\text{'R-weighted pattern'})$$

$$S = \left\{ \frac{S_y}{(N-P)} \right\}^{1/2} = \frac{R_{wp}}{R_e} \quad (\text{'Goodness-of-fit' indicator})$$

$$\text{where } R_e = \left\{ \frac{(N-P)}{\sum w_i (y_i(obs))^2} \right\}^{1/2} \quad (\text{'R-expected'})$$

$$DW = \frac{\sum_{i=2}^N (\Delta y_i - \Delta y_{i-1})^2}{\sum_{i=1}^N (\Delta y_i)^2} \quad (\text{'Durbin-Watson' statistic})$$


This slide shows the mathematical expressions of some of the numerical agreement factors. The pattern residual and the weight of pattern residual describe the agreement between the observed and calculated pattern at each data point in the profile. The residual pattern is therefore much affected by the signal to noise ratio, the background noise level. The residual weighted pattern therefore accords a bit more weight to the actual signal or the peaks to mitigate the dependence but still it is much influenced by the quality of the data. To remove this dependence entirely one can use the goodness-of-fit indicator that normalizes the weight of pattern residual by an expected residual. This expected residual is an index that is calculated for a best achievable data fit of the data. While the pattern residual and the weighted pattern residual should reduce as much as possible during the fitting, the goodness-of-fit indicator should obviously converge to a ratio of one. On the other hand, there is the Durbin-Watson statistic, and this is applied to residuals of least squares analysis to detect any waves of auto-correlation between the data. If the value is close to two, then there are no indications of auto-correlation. If they are actually indications of auto-correlation, then measures to increase the signal to noise ratio or resolution should actually be considered.

Notes

Summary



5m 09s



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We thank Crystal Impact GbR for their financial support of the publication "Crystallography Open Database - an open-access collection of crystal structures", *J. Appl. Crystallogr.* (2009) PDF version.

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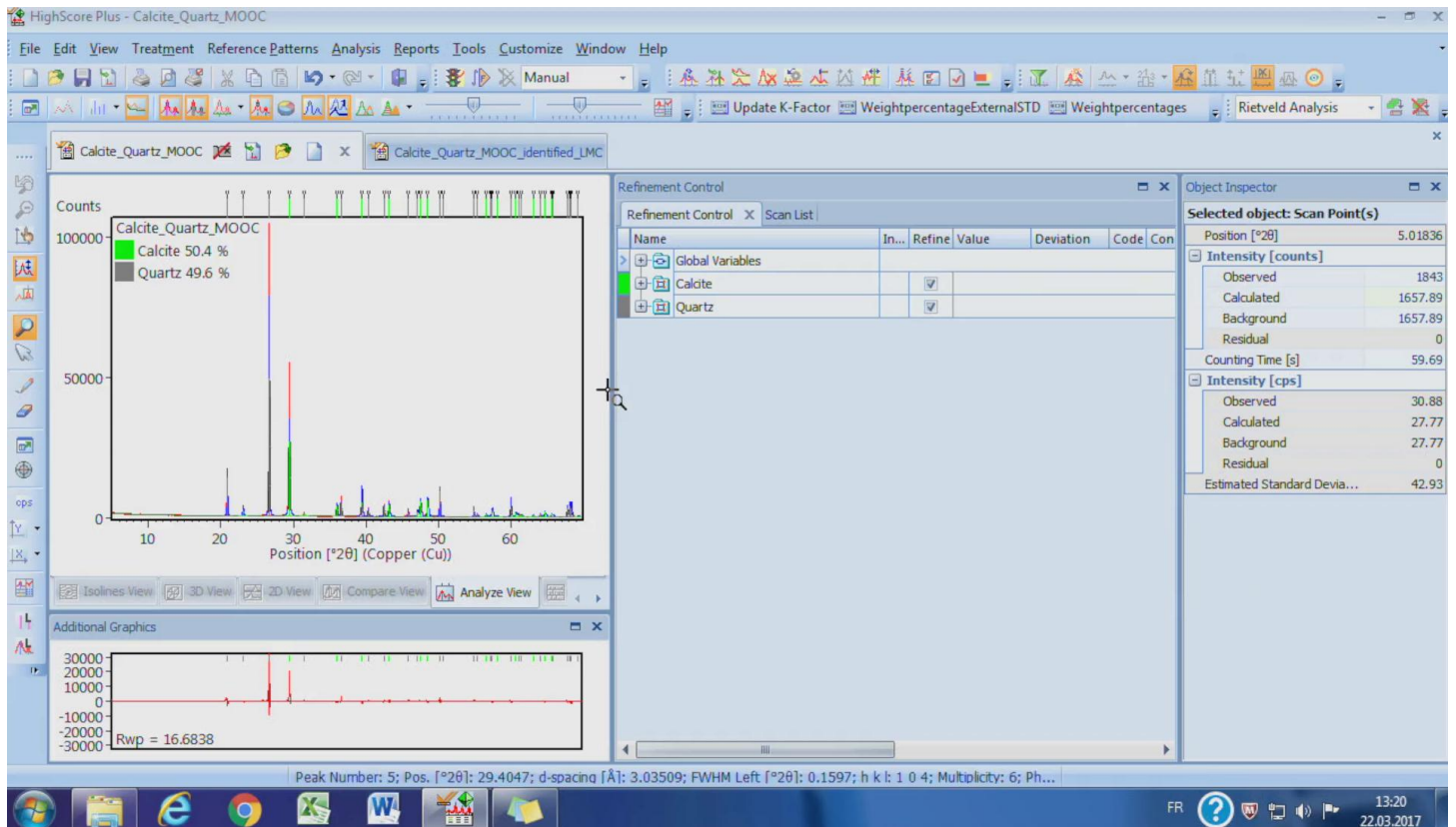
Let's have a look at how the Rietveld fitting operates in practice. We will show you some snapshots of a Rietveld refinement over a simple two phase material consisting of alite and rutile. To continue with the Rietveld method we should have already done the identification. With the results from the identification the related crystallographic information file, namely the “C file” must be found to perform the Rietveld analysis. The file can be found in the commercial database such as the Inorganic Crystal Structured Database (the ICSD), or the open database such as the Crystallography Open Database, (the COD).

Notes

Summary



6m 40s

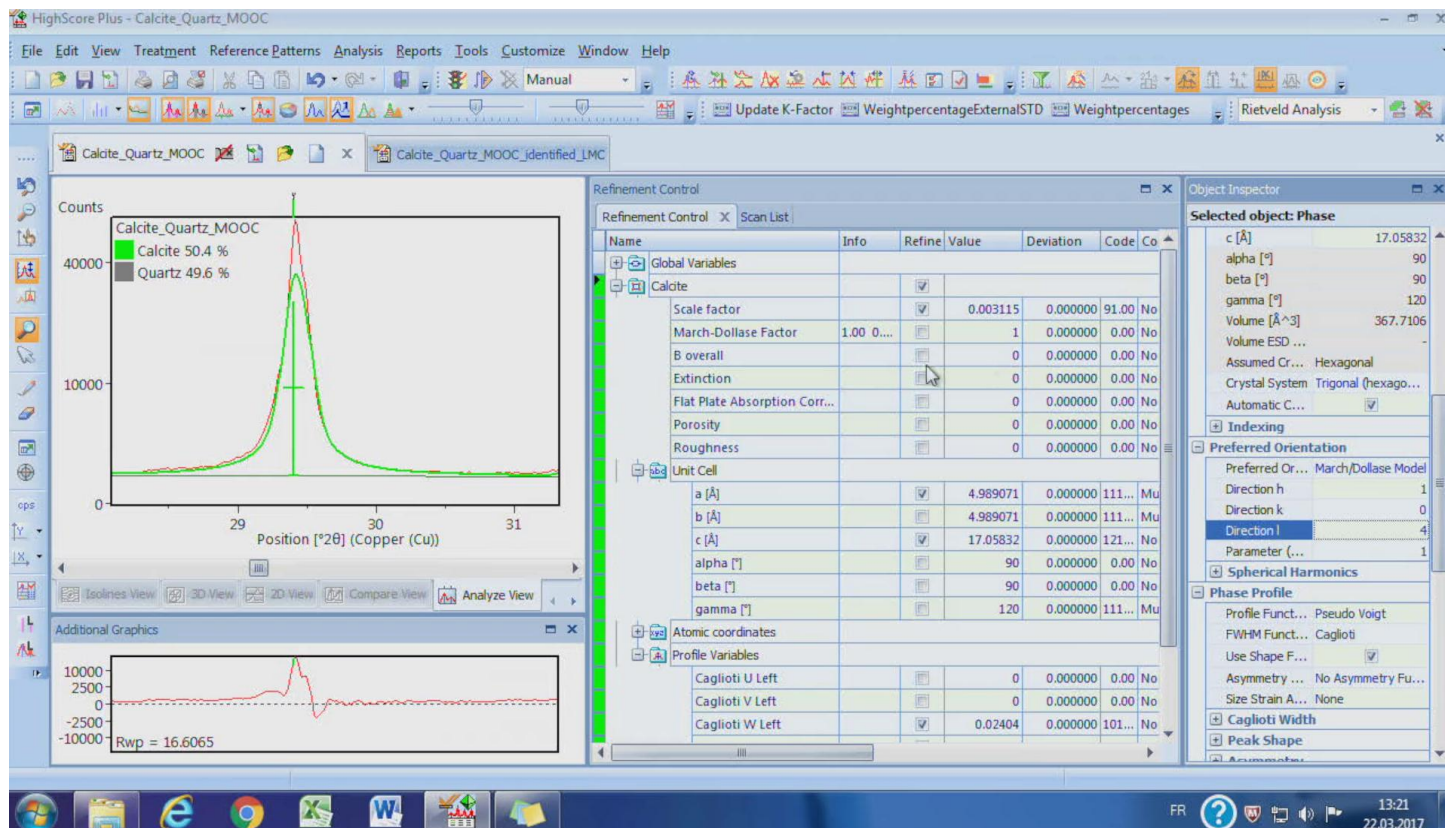


First, create a new file, then insert the data. According to the identification we did before, the mixture is made of calcite and quartz. Firstly, we import the structures. Let's change the name, calcite and then quartz. For each phase the scale factor, units cell and profile should be refined. Constraints of 1% of variation on the unit cell were applied to secure refinements. Another constraint for the profile W of 0.0001 to 0.2 was applied. The application of constraints to the refined parameters will improve the stability of the overall refinement when especially we are analyzing complex samples, such as the hydrated cement. Do the same settings for the quartz phase. For global parameters, the specimen displacement, background functions are refined. For the background functions, we use the polynomial function together with a flat background, 1 over x together with a fifth five, together with a five coefficient. We use the manual mode for the refinement as we set the parameters manually. After all the parameters are set, the refinement can be executed. Open the additional graphics for the difference plot to visually check the fitting. Change the y-axis to square root to show more details on the small peaks.

Notes

Summary



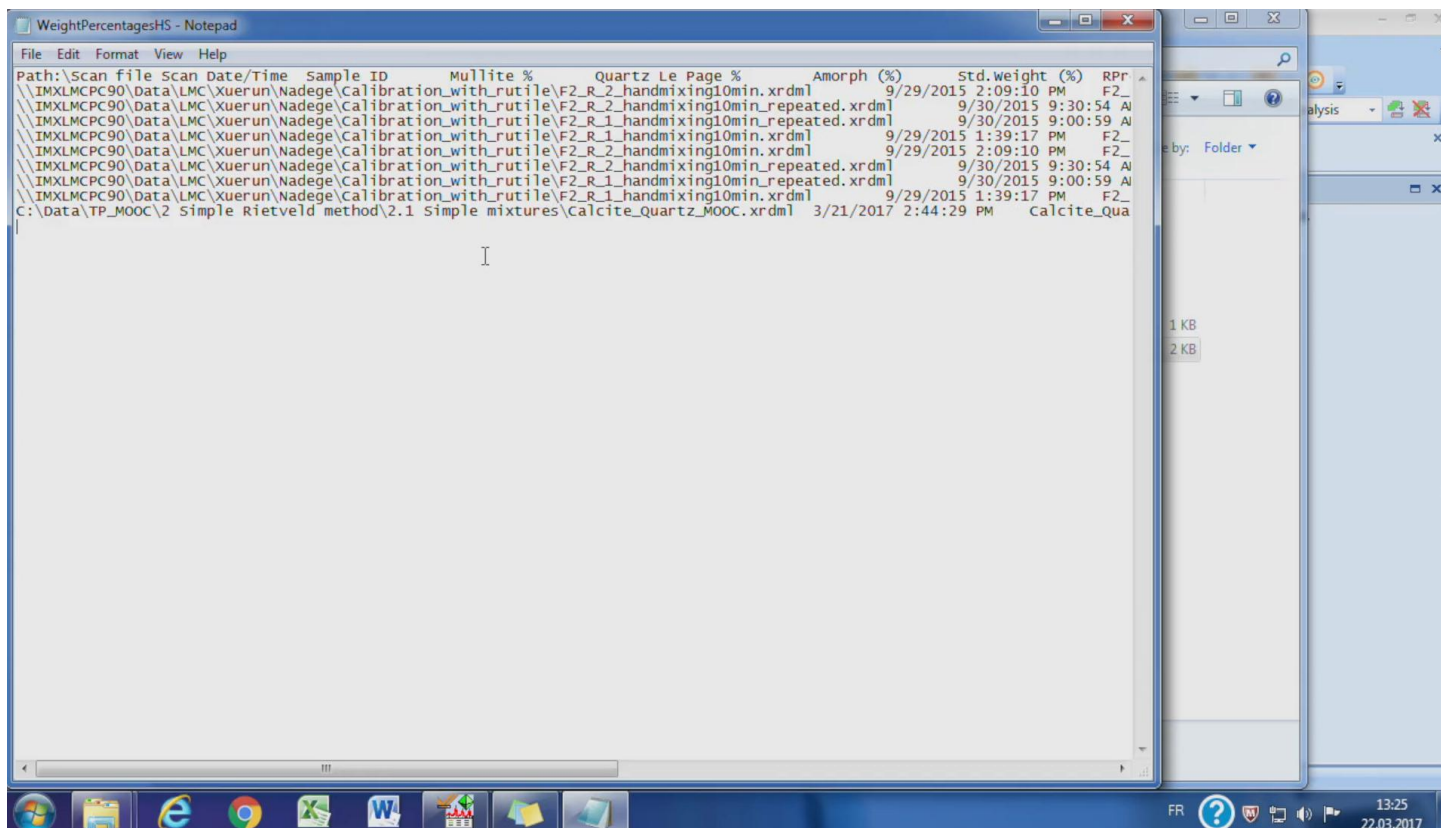


You can evaluate the fitting by checking the agreement indices, namely the R profile, weighted R profile and the goodness-of-fit. The aim of the refinement is to decrease the residue of the fitting, thus the value for R profile and weighted R profile should be lower to be better. Typically, 5 to 15 percentage for the weighted R profile is acceptable for most cases. Theoretically, the goodness-of-fit should be 1. Practically, a value of 1 to 5 can be acceptable depending on the case. Now the goodness-of-fit is 5.9 and the weighted R profile is 16.6. If we check the residue plot, the fitting at around 27 and 30 degrees is not so good and this can be because of the preferred orientation. If you locate the mouse on the peak which is not well fitted, the crystal plane of the peak will appear along with the name of the phase. Here it is a 104 plane for calcite. To set the preferred direction, you can click on the calcite in refinement control, then in the object inspector for calcite you will find the item called 'preferred orientation'. The March/Dollase model is recommended. Specify the direction h, k, l of the plane for the preferred orientation. After setting the direction, check the refine for the March/Dollase factor.

Notes

Summary





Similarly to the other parameters, we put a limit for the refinement of 0.7 to 1. The value 1 means there is no preferred orientation, the smaller the value is the higher the preferred orientation. In most cases 0.7 should be enough. If the value is too small, it means that the sampling is not well done. A repetition of the XRD data collection with more attention on reducing the preferred orientation is recommended. By refining, the fitting of the peak is much improved. Do the same for the preferred orientation of quartz. The plane of the quartz is 1 0 -1, and then refine. There is some improvement for the goodness-of-fit and the weighted R profile. As you can see, there are still some misfitting for the peaks of calcite and quartz. For calcite and quartz binary mixture, to achieve better fitting, more profile parameters need to be used. Let's try all the profile parameters for quartz, and calcite. Refine again. The fitting is much improved by using more profile parameters and the calculated weight percentage for the calcite and quartz are getting closer to the weighed amount. Save the HPF file, click on "weight percentages", you will have the quantitative data output in text files in the default HighScore plus folder. Or simply note down the results from the graphic window.

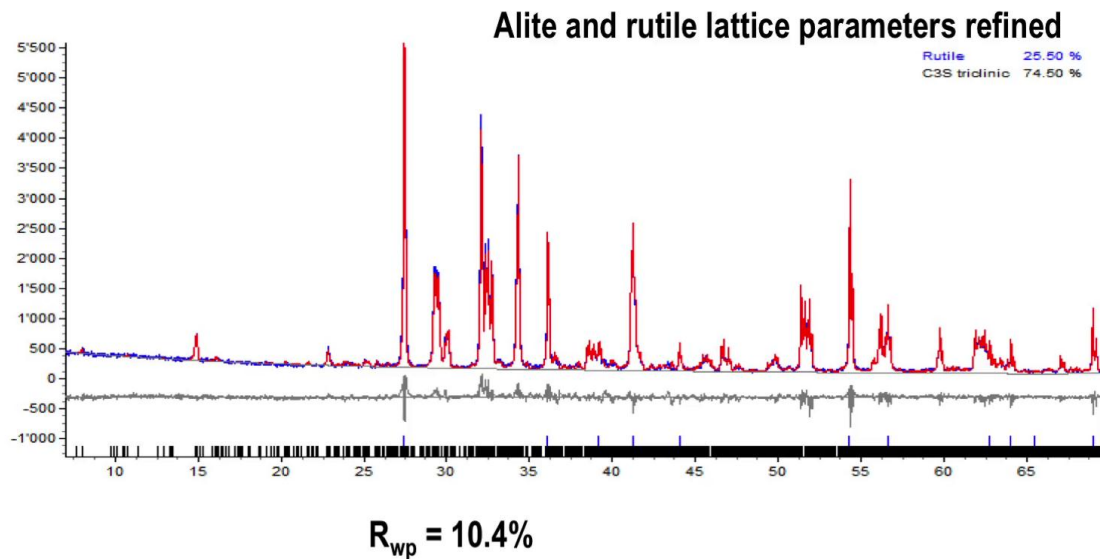
Notes

Summary

10m 33s



The Rietveld method – simple fitting example



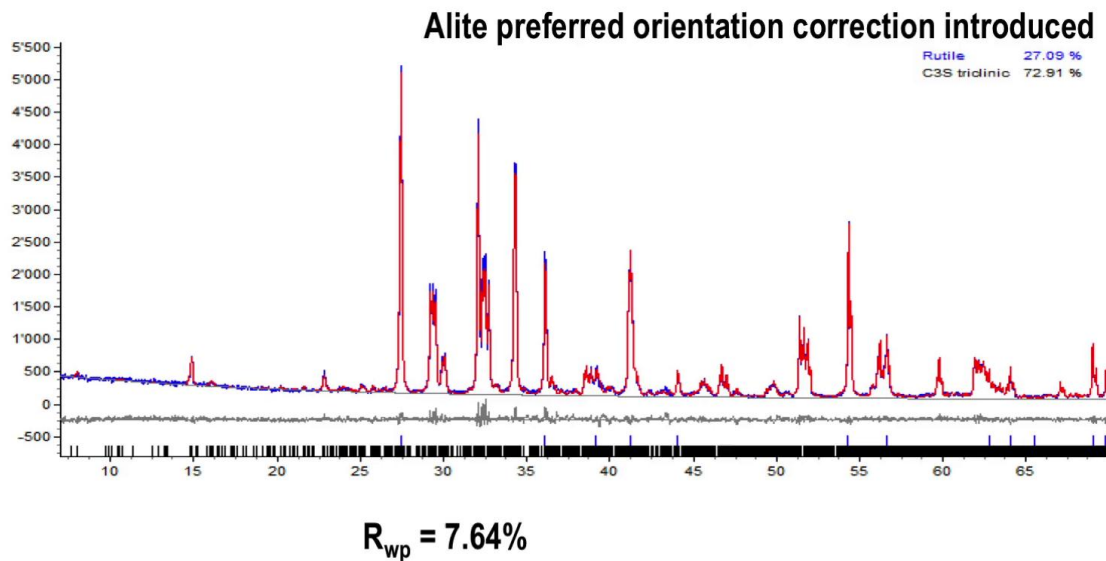
This is our X-ray diffraction scan. Measure it on a conventional lab diffractometer, using copper K alpha radiation. We can see a multitude of peaks, some single, others overlapping. In a first try, a background function is fitted, and the first residual is calculated as you can see below the graph. Obviously, this residual is still very high because we have not fitted any of the red peaks. In a second step, we introduce rutile into the fitting procedure. Now you can see that only the intensities or the peaks of the rutile are being fitted, and this is done by adapting the scale factor. You can see that the residual has decreased. Then we will introduce alite as triclinic, tricalcium silicate into the refinements. Again you can see that only the intensities of the alite are fitted and the agreement index drops again, but you can clearly see that there is still a visual mismatch of some of the alite peaks. We then allow the alite and rutile lattice parameters to be refined together. Together with the scale factors of each as well. Now, we clearly see that the weighted pattern residual drops drastically and that there is already quite a good fit when looking at the residual.

Notes

Summary



The Rietveld method – simple fitting example



This residual curve in gray below, the diffraction scan, help us spot slight mismatches and see where there is some deviations from the fit. Now we also refine the next step, the peak width for both alite and rutile. Again you can see that this significantly improves the fitting both in the residual as in the visual appearance. Further fine tuning of the Rietveld refined can now be done. For instance, by adding the atomic displacement factors from the literature data. Then finally we can include a preferred orientation correction for the alite phase to achieve our final fitting results. One can now see that the fitting is really nice and that the residual curve is quite flat. In the case of this sample, we then actually have about 27 percent of rutile and about 73 percent of C3S, triclinic C3S, in this mix. This example shows that the parameters that we vary in quantitative phase analysis are first so-called global parameters such as the background and a sample displacement correction and then second phase specific parameters, such as scale factors that will fit to the observed peak intensities, unit cell parameters that will fit to the peak positions, and peak profile functions that will fit to the shape of the peak.

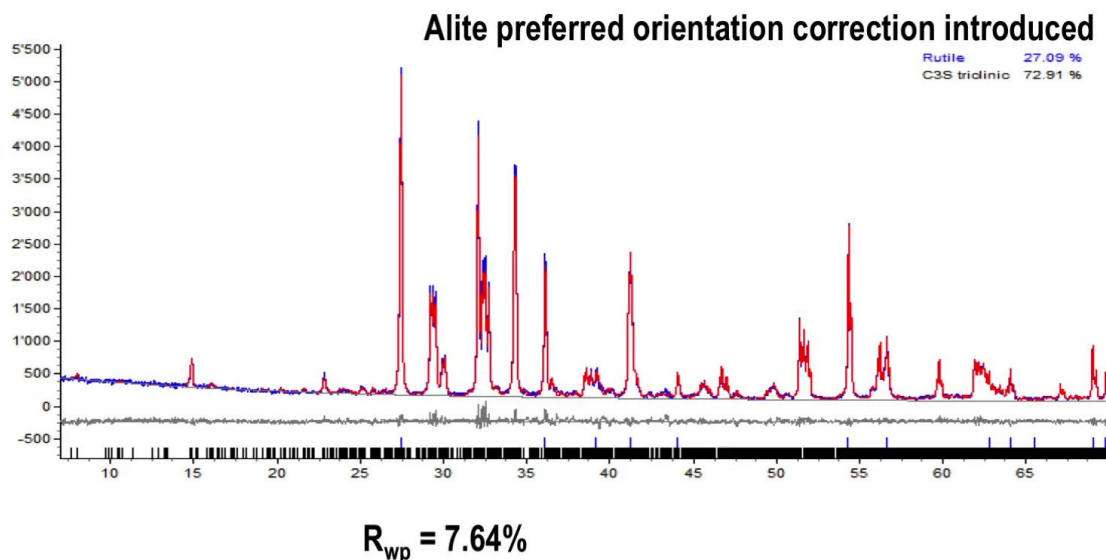
Notes

Summary



13m 41s

The Rietveld method – simple fitting example



The use of intensity corrections such as preferred orientation functions may be necessary but will be included later in the refinement always. The refinement of other crystal structure parameters such as atomic positions, sites occupancies or atomic displacement parameters is not recommendable for complex mixtures of phases such as cements. This is because this may lead to wrong results due to strong correlations and parameter variations during the fitting as the ratio between variables and independent data strongly decreases, and the minimization problem gets under constraint.

Notes

Summary



15m 11s